

Silatronix

High-performance
organosilicon compounds
for energy storage

New Advanced Stable Electrolytes for High-voltage Electrochemical Energy Storage

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Project ID: ES271

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Overview

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Timeline

- Project start date: 10/01/2015
- Project end date: 09/30/2017
- Percent complete: 25%

Budget

- Total project funding: \$ 1,665 K
 - DOE share(Silatronix): \$897 K
 - Contractor share: \$333 K
- Budget Period 1(FY16): \$662 K
- Budget Period 2(FY17): \$235 K

Barriers

- Electrolyte development for
 - High voltage stability
 - Good thermal stability
 - Stable SEI layer to improve cycle life

Partners

- US Army Research Laboratory
- Argonne National Laboratory

Objective and Relevance

Project Objective: Develop an electrolyte system stable at high voltage ($\geq 5\text{V}$) to enable the development of high energy density Li-ion batteries required by the automotive industry.

Relevance: This technology, if successful, will have a significant impact on the enablement of high voltage cathode materials in Li-ion battery technology. This in turn will provide a significant pathway for the development of higher energy density electrochemical storage devices, which is critical to expanding the electrification of the US vehicle fleet.

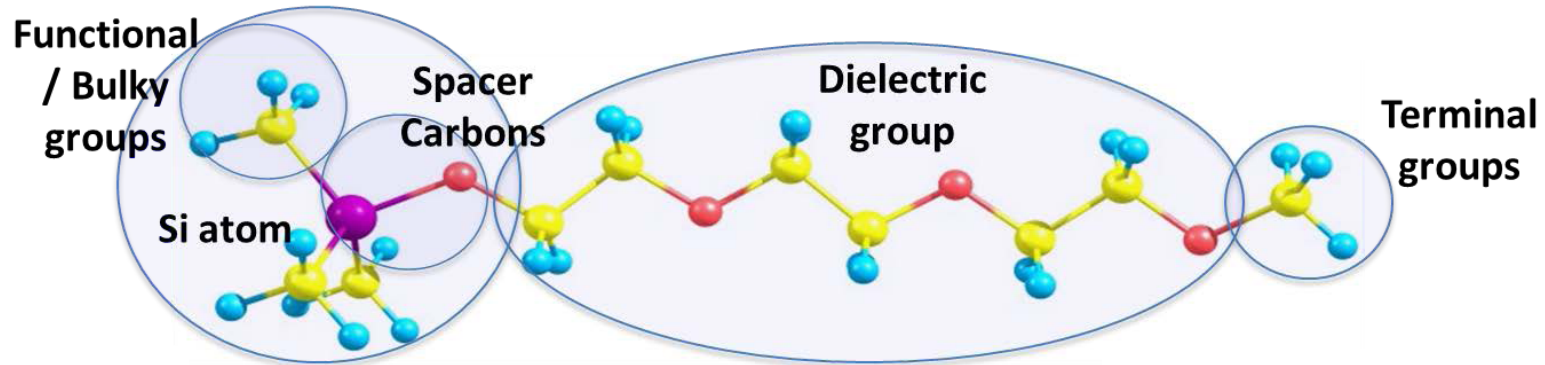
Specific Technical Metrics:

- Oxidative Stability
 - Breakdown voltage $> 6\text{ V}$ (vs. Li/Li^+)
 - Parasitic current $< 0.02\text{ mA/cm}^2$ (at 6 V and 50°C)
- High Voltage System Performance
 - Initial capacity \geq carbonate control (e.g. 5V LNMO system)
 - Initial capacity left $> 80\%$ (300 cycles at $\geq 55^\circ\text{C}$)

Background: Organosilicon Solvents Can Be Engineered with Targeted Characteristics

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General Organosilicon (OS) Structure



- Each group in OS structure adds specific capability for performance.
- Dozens of unique structures have been synthesized and characterized for physical characteristics, stability in electrolyte formulations, and cell performance benefits.
- **OS stabilizes entire electrolyte by protecting LiPF_6 from decomposition.**
 - **OS3 protects LiPF_6 from decomposition through solvation mechanism.**
 - Elimination of reactive decomposition products protects all electrolyte and battery components.
 - Benefits demonstrated at low OS3 content (< 5%).

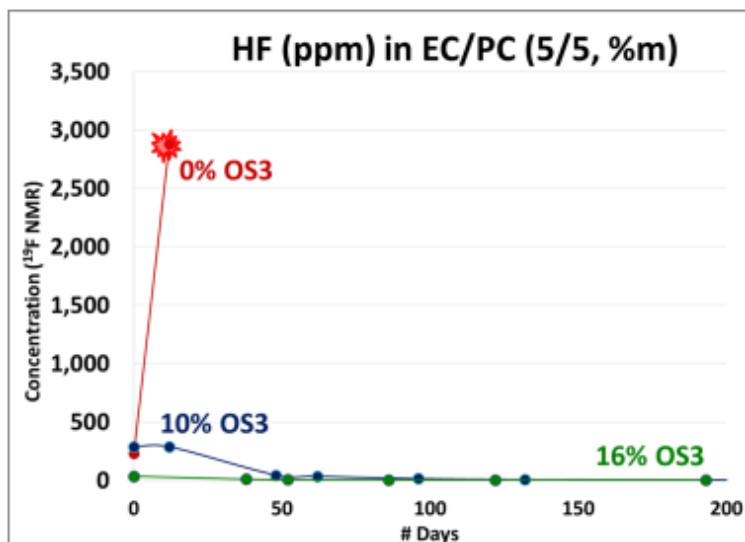
Background: Organosilicon Solvents Provide Electrolyte Stability Benefits

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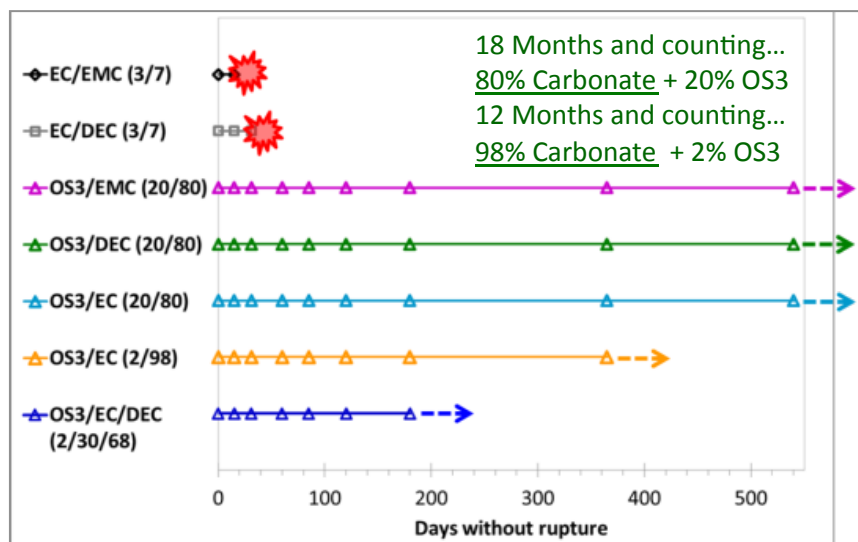
OS3 enhances thermal stability of 1M LiPF₆ electrolytes without additives

- Suppresses formation of HF and PF₅ from LiPF₆ decomposition.
- Reduces decomposition of carbonate solvents and formation of CO₂.
- Unlike additive, OS3 is not consumed in order to provide it's benefits.

HF Suppression during 100°C Storage



Reduced Gas Generation during 100°C Storage



OS3 reduces HF formation by preventing PF₆ decomposition in carbonate electrolytes.

Addition of 2-20% OS3 to carbonate electrolytes prevents decomposition and sample failure.

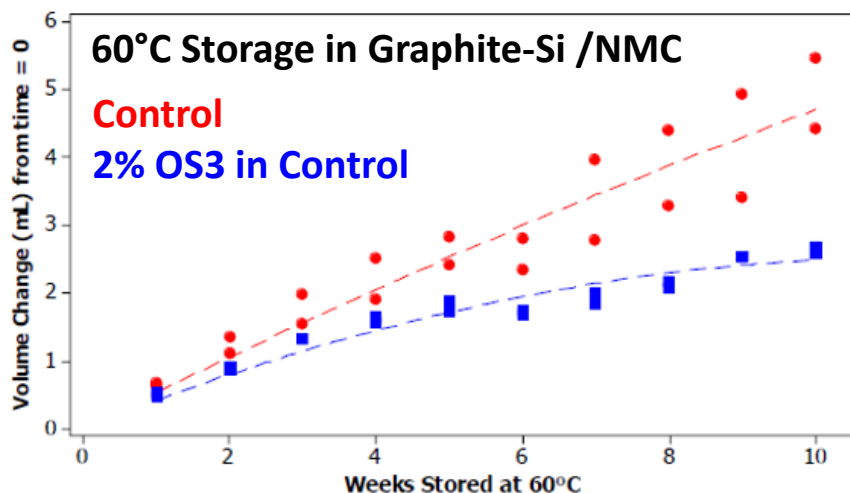
Background: Organosilicon Solvents Provide Fundamental Stability Advantages

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OS3 formulations have shown a number of tangible benefits

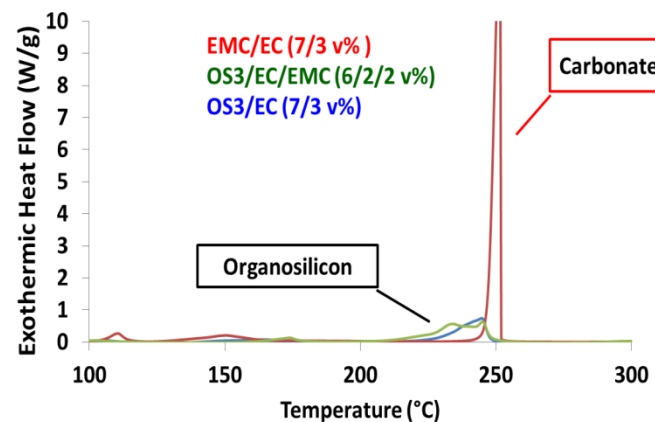
- Reduces swelling in pouch cells at temperature.
- Improves cycle life and capacity retention at temperature.
- Improves safety profile of reactive cathode systems.

Reduced Gas Generation in Pouch cells



2% OS3 electrolyte demonstrated 50% less gas generation during 60°C storage at 100% SOC.

Enhanced Abuse Tolerance with LNMO Cathode



DSC of de-lithiated cathode with OS3 electrolyte shows much lower heat output compared to carbonate electrolyte.

Project Milestones

Milestones for Budget Period 1:

Milestones and Go/No-Go Decision	Milestone Verification Process	Date	Status
Baseline characterization: Oxidative breakdown of control electrolytes	Linear scan voltammetry and cyclic voltammetry at Silatronix	Nov. 2015	Complete
Characterize synthesized LCP	Verify structure and purity of LCP by ARL	Jan. 2016	Complete
Characterization of 2-3 new HV OS solvents/additives	Purity (>98%) and H ₂ O (<20ppm) by Silatronix	Apr. 2016	In Progress
Go/No-Go Decision: Feasibility of HV performance demonstrated in ref. cells through determination of oxidative breakdown	Lin. scan voltammetry (>6V); Parasitic current 4.5-6.5V at 50°C (<0.02 mAh/cm ² at 6V) at Silatronix	Jun. 2016	In Progress
New HV OS solvents /additives synthesized	NMR verification of structures (4-6) by Silatronix	Aug. 2016	In Progress
New HV co-solvents /additives synthesized	4-6 compounds prepared at ARL	Sep. 2016	In Progress
Electrochemical evaluation, analysis, and diagnosis of new materials	CV, EIS, leakage current in half-cells	Sep. 2016	In Progress

Technical Progress: Fundamental Mechanistic Studies of New Electrolyte Materials

- Silatronix synthesized four organosilicon solvents (OS3, OS3a, OS3b, OS3c) in the OS3 family that have the potential to show high oxidative stability.
 - Approach: stability and performance of organosilicon (OS) solvents can be optimized to address specific application metrics via rational molecular design.
- ARL synthesized 8 new additives with bifunctional groups for protection of both anode and cathode surfaces. Testing has begun with two additives at Silatronix. ARL finished the characterization of lithium cobalt phosphate (LCP) cathode, which significantly improved the performance both in terms of discharge profile and cycling stability.
- Silatronix characterized new HV materials and investigated their fundamental electrochemical behavior.
 - Approach: LSV, Parasitic current, and other analytical techniques are utilized to determine the oxidative breakdown voltage and mechanism of breakdown.

Technical Progress: Preliminary Screening of OS Solvents

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OS3 Family vs Control: Physical Properties

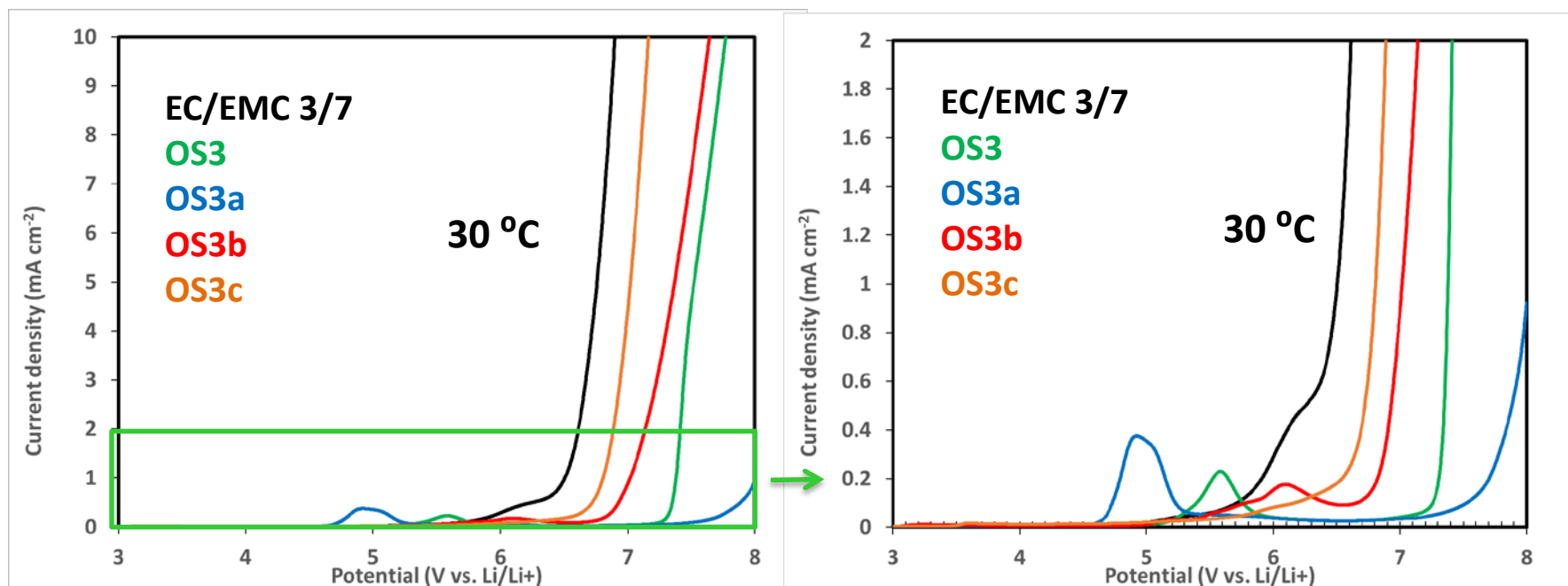
Solvents	Neat Solvent Properties			Electrolyte Properties (w/1M LiPF ₆) at 30 °C	
	Dielectric	Flash Pt (°C)	Density (g/cc)	Conductivity (mS/cm)	Viscosity (cP)
OS3	16.8	82	0.93	2.8	8.0
OS3a	12.6	72	0.81	1.6	9.4
OS3b	18.2	78	1.09	3.5	7.9
OS3c	19.5	64	1.10	5.0	6.8
EC/EMC (3/7)	22.1	<30	1.10	10	3.1

All OS3 family solvents provide significantly higher flash points than carbonate control, with good conductivity and viscosity in electrolyte blends.

Technical Progress: LSV of New OS Electrolyte Materials

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LSV of OS3 Family Solvents at Pt Electrode (OCV to 8 V), all with 1M LiPF₆ salt. (Test Condition: 30°C)

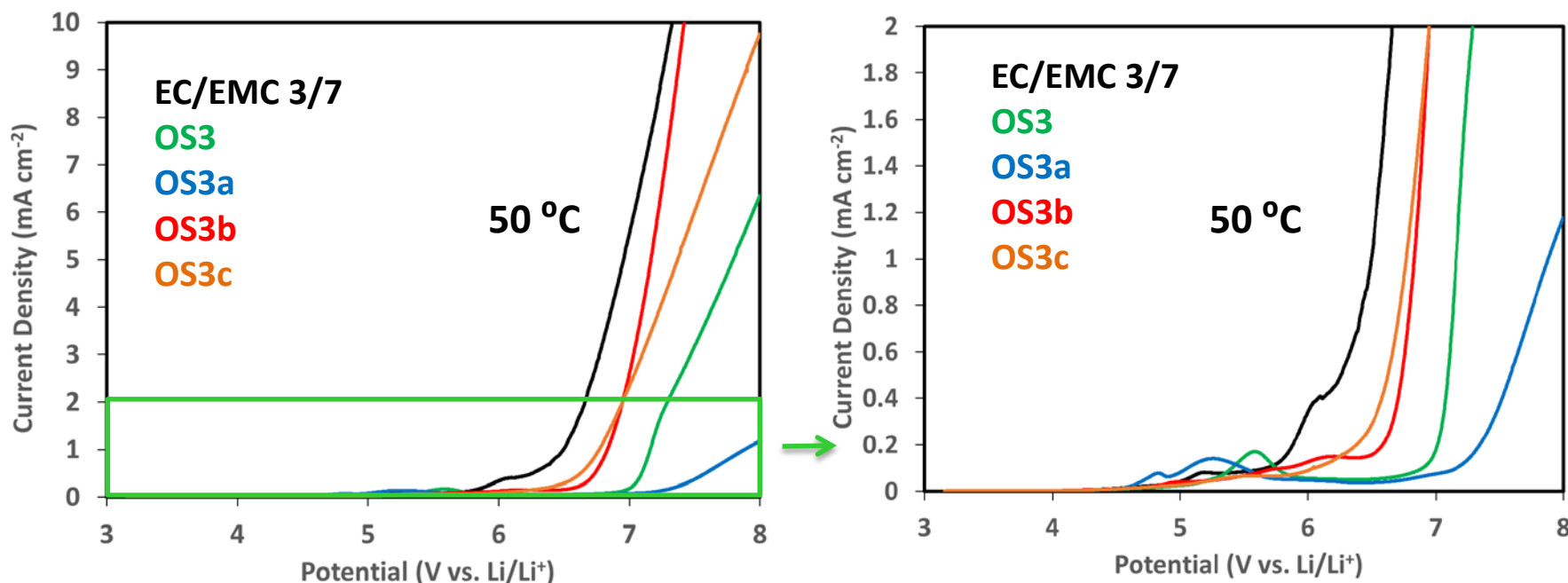


All OS solvents show higher breakdown voltages than carbonate controls. The investigation of small oxidation peaks before breakdown is in process.

Technical Progress: LSV of New OS Electrolyte Materials

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LSV of OS3 Family Solvents at Pt Electrode (OCV to 8 V), all with 1M LiPF₆ salt. (Test Condition: 50°C)

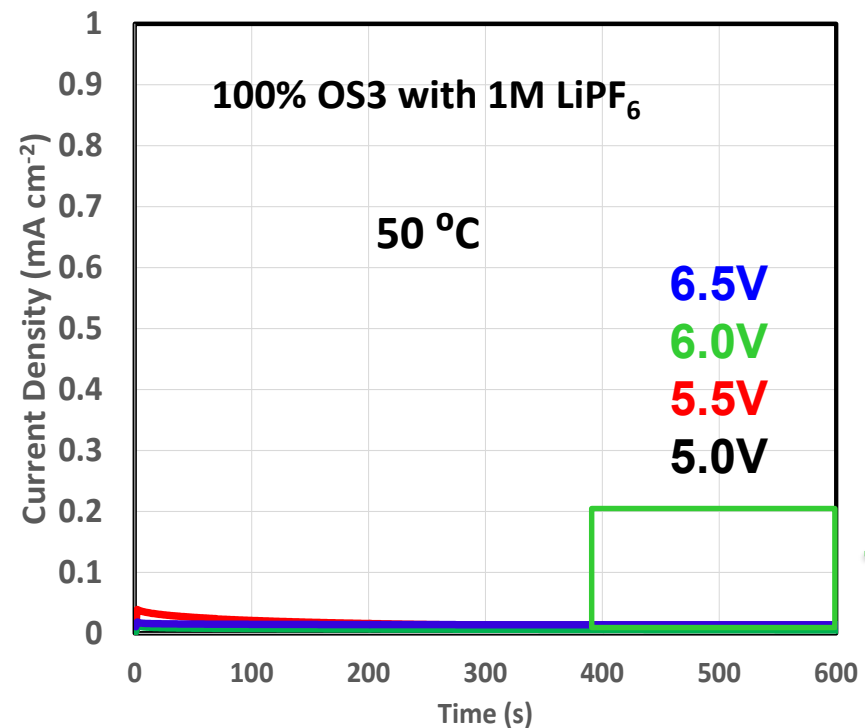
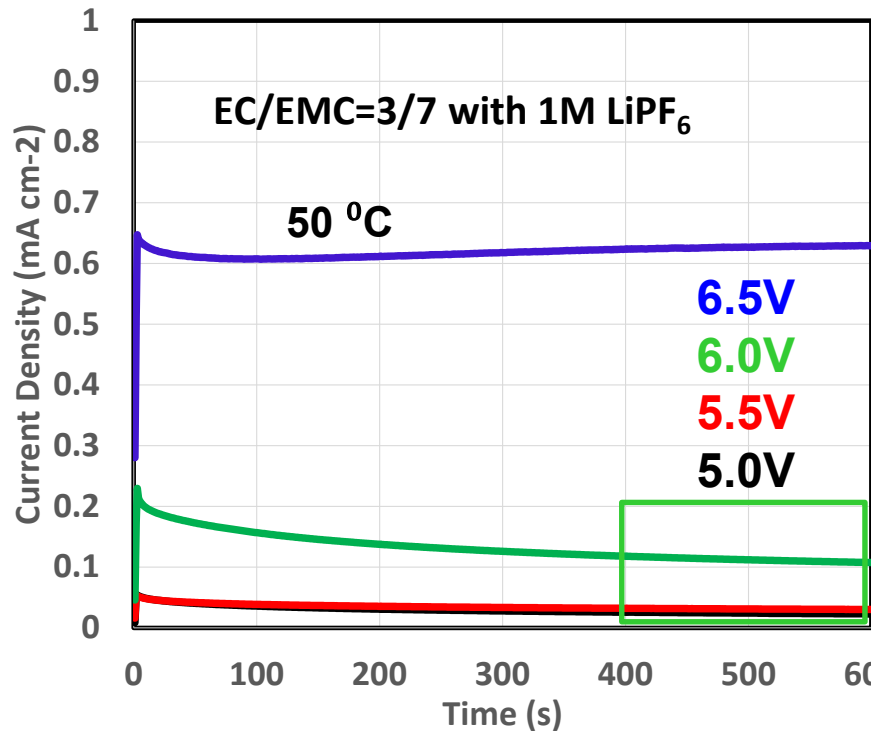


Similar trend have been observed for OS solvents at 50°C, which show better oxidative stability than carbonate control.

Technical Progress: Floating Test of New Electrolyte Materials

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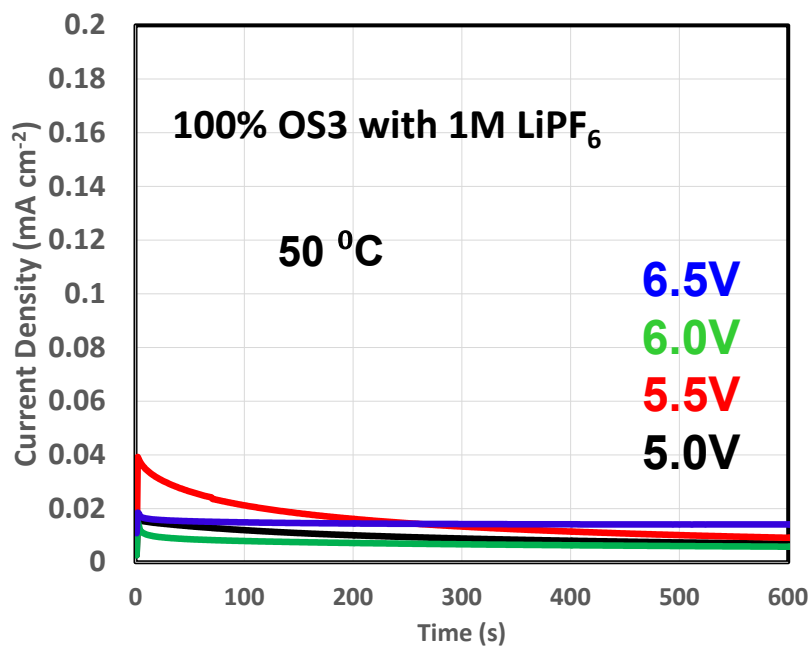
Floating Test of Carbonate control and OS3 at Pt Electrode
(4.5-6.5 V, 10 min at each voltage. Test Condition: 50°C)



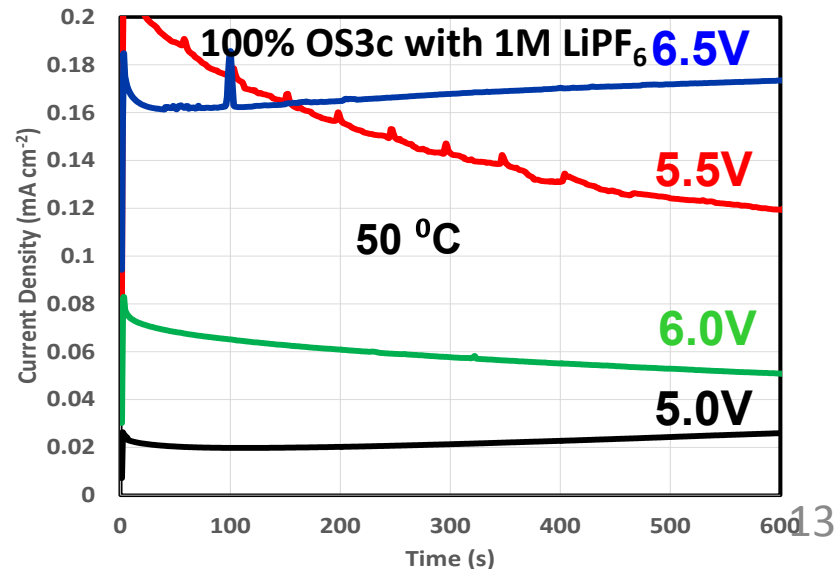
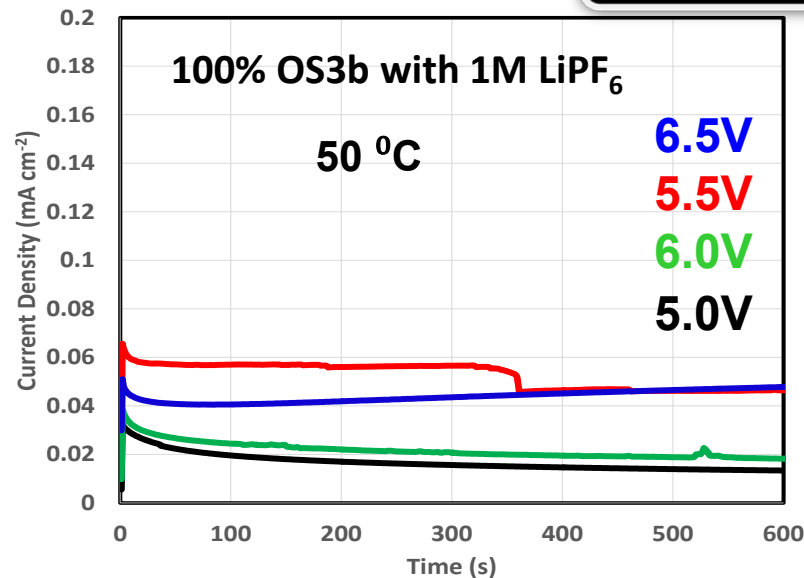
Technical Progress: Floating Test of New Electrolyte Materials

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Floating Test of Carbonate control and OS3 at Pt Electrode (4.5-6.5 V, 10 min at each voltage. Test Condition: 50°C)



Parasitic current from OS3 is lower than 0.02 mA/cm² at 50°C (technical metric), OS3b and OS3c are still much lower than control above 6V.

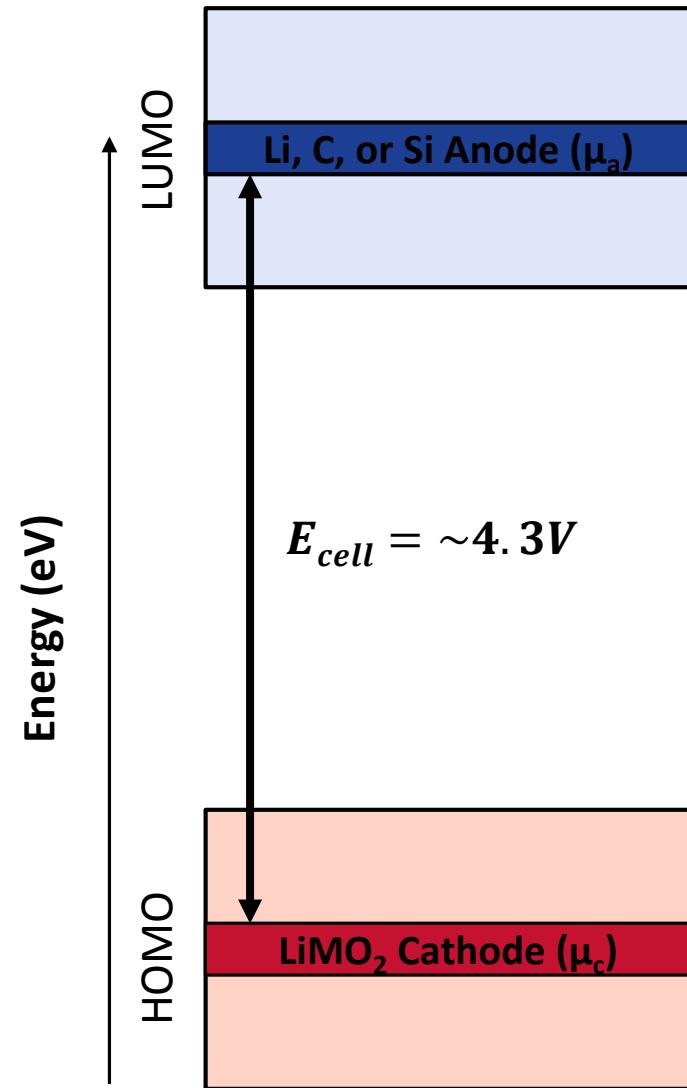




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Strategy for Additive Development

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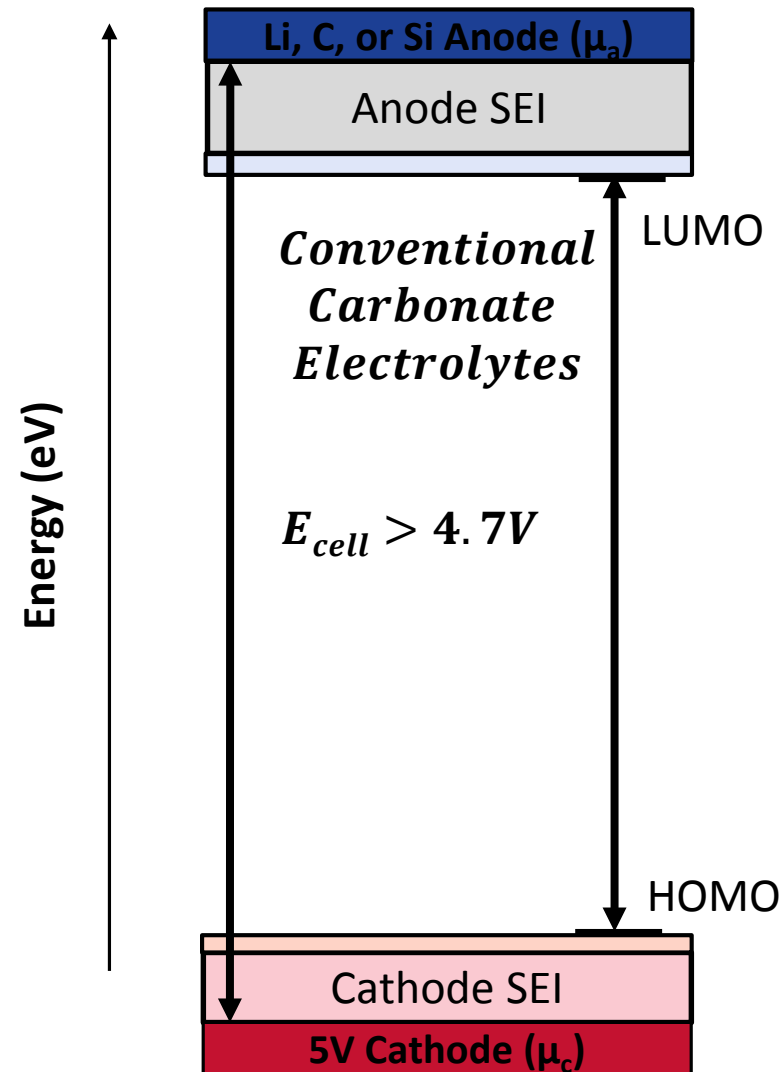




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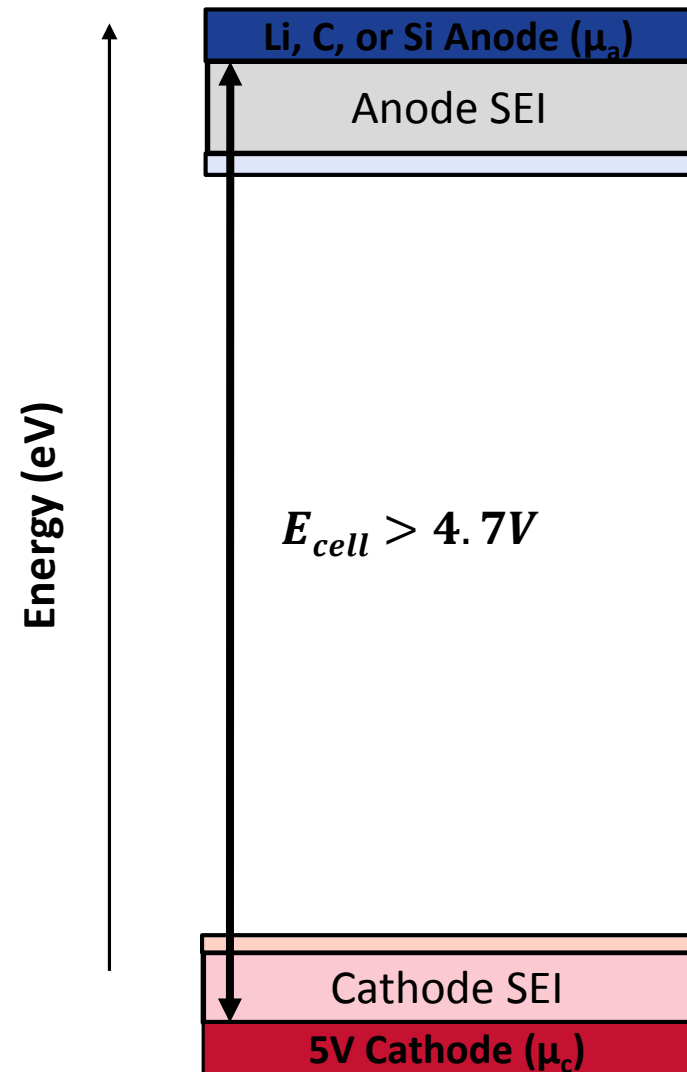
Strategy for Additive Development

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Strategy for Additive Development

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- Molecular engineering to expand stability window of baseline electrolytes with additives (<5 wt%)
- Tune electrode-electrolyte interface chemistry to support high voltage (>5V) electrode couples
 - New solvents with intrinsic stability
 - Self-limiting sacrificial interphase
 - Redox shuttle
- Manage oxidative stability of electrolyte without compromising other critical properties
 - Salt solubility
 - Ionic conductivity
 - Temperature stability
 - Safety

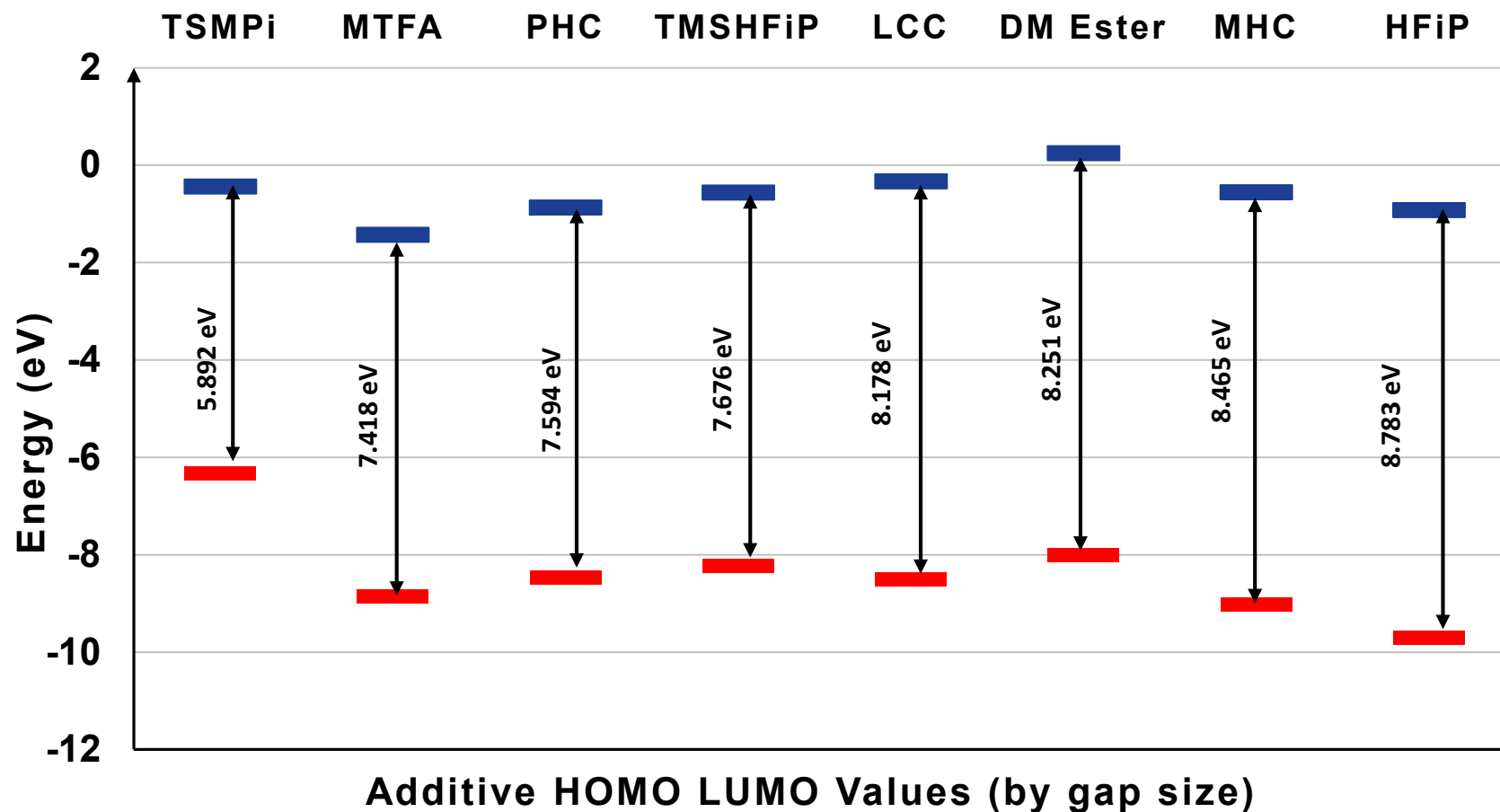
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HOMO-LUMO as QC Guide

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Holistic Design Approach:

Key functional groups effective in forming cathode and anode SEI are synthetically integrated in each additive chemistry



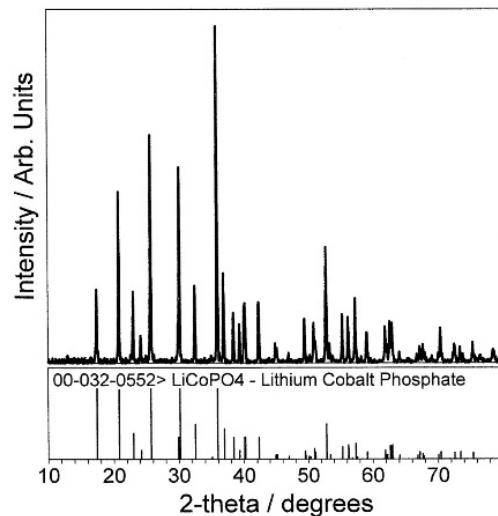
***Reduction and oxidation potentials cannot predict consequent interphase chemistry



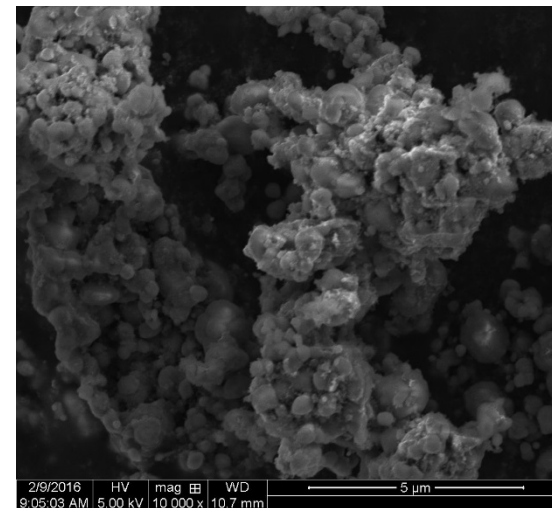
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Subst'd LiCoPO₄ Characterization

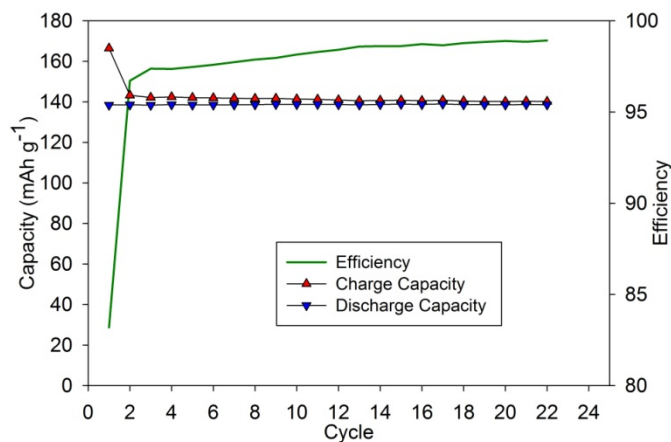
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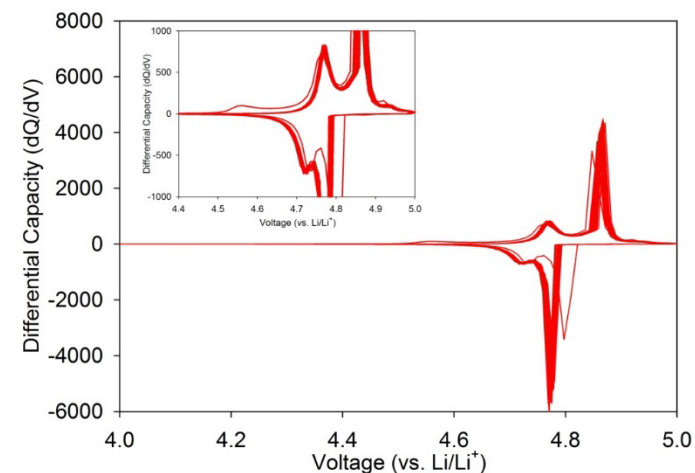
X-Ray Diffraction confirms
Phospho-olivine structure



SEM : ½ micron particle size
BET surface area: 4.4 m² g⁻¹



Stable discharge capacity in baseline electrolyte
1.2M LiPF₆ in 3:7 EC:EMC + 2 wt.% additive

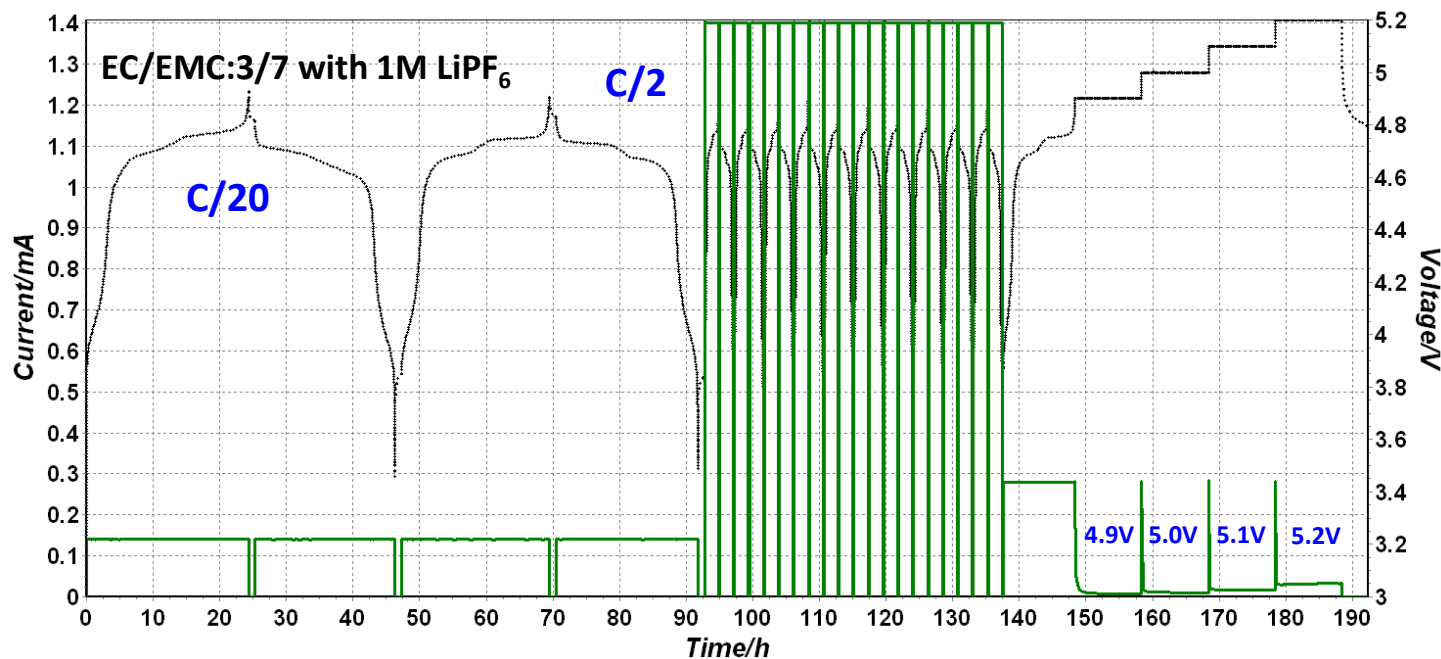


Stable discharge voltage in baseline electrolyte
1.2M LiPF₆ in 3:7 EC:EMC + 2 wt.% additive

Technical Progress: Development for Specific HV Systems

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- ANL provided 5V LNMO cathode and graphite anode for laboratory testing at Silatronix and ARL.
- Silatronix utilized cathode half cells to determine the fundamental behavior of the new materials with the 5V LNMO system.

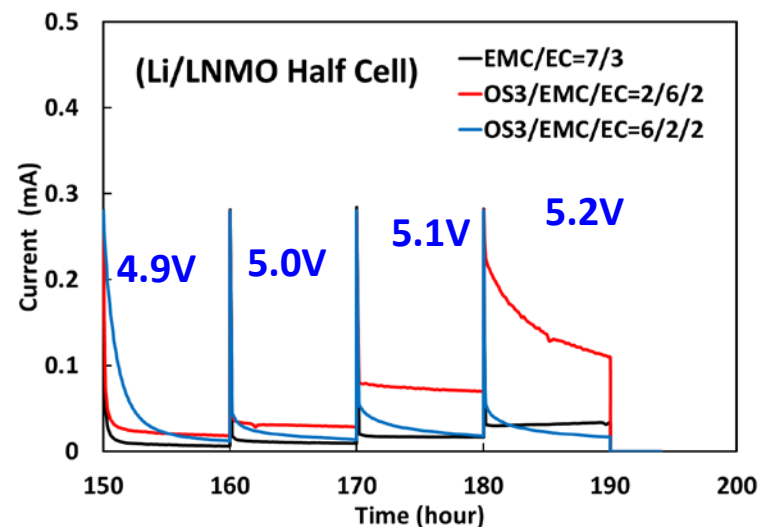
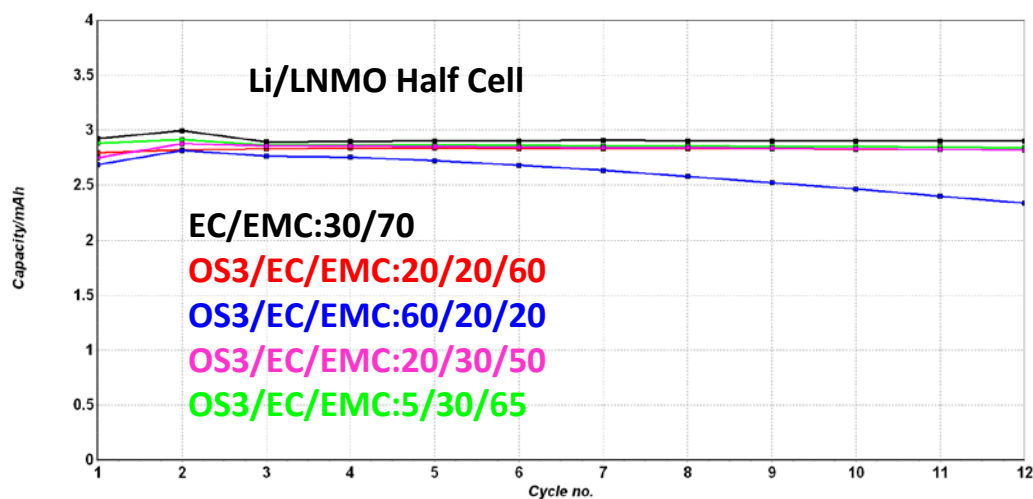


Method: Cathode half cells (LNMO/Li) are cycled at C/20 for 2 cycles (3.5-4.9 V) and C/2 for another 10 cycles (3.5-4.9 V), then charged at C/20 again to 4.9V, hold for 10h at each voltage until 5.2V.

Technical Progress: Initial Evaluation of OS Formulations (without additives) in Li/LNMO Half Cell

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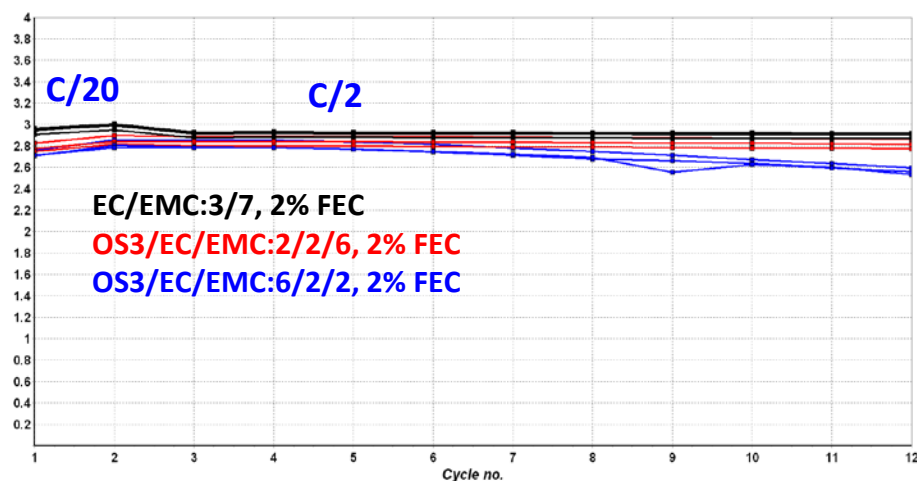
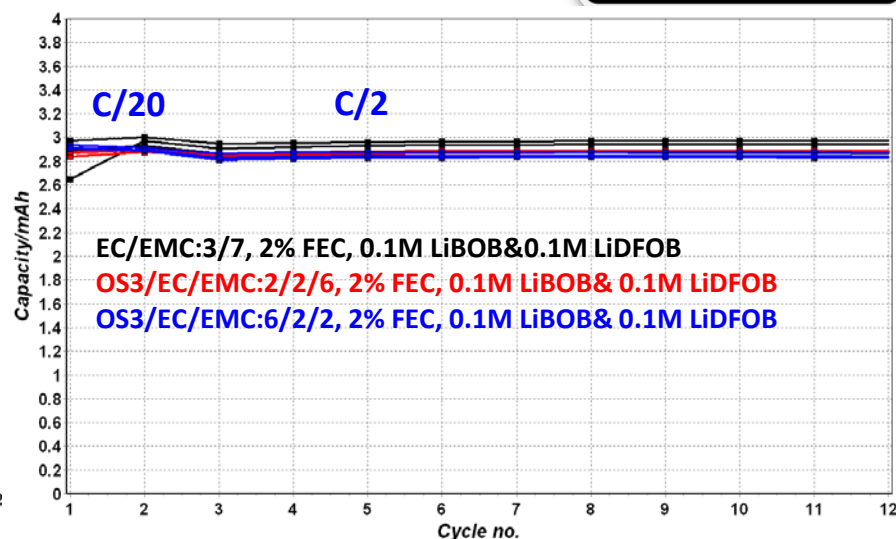
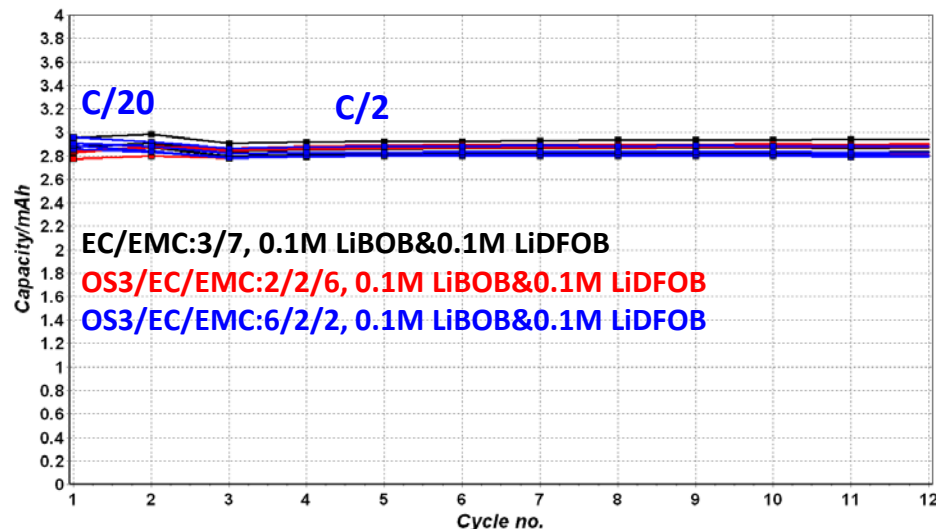
Cycled at C/20 for 2 cycles (3.5-4.9 V) and C/2 for another 10 cycles (3.5-4.9 V).



Different OS3 formulations ($OS3 \leq 20\%$) show similar performance compared to carbonate control; 60% OS3 shows better stability at 5.2 V and requires appropriate additives to improve cycling performance.

Technical Progress: Cycling of OS Formulations(with Additives) in Li/LNMO Half Cell

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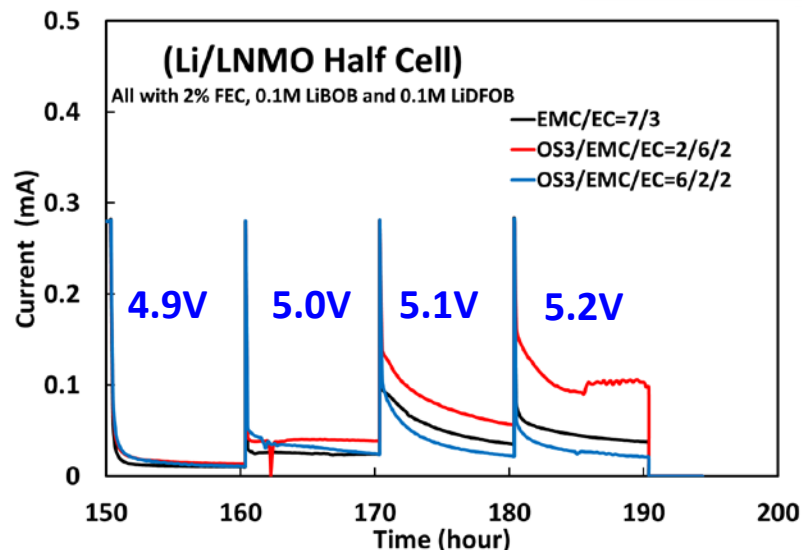
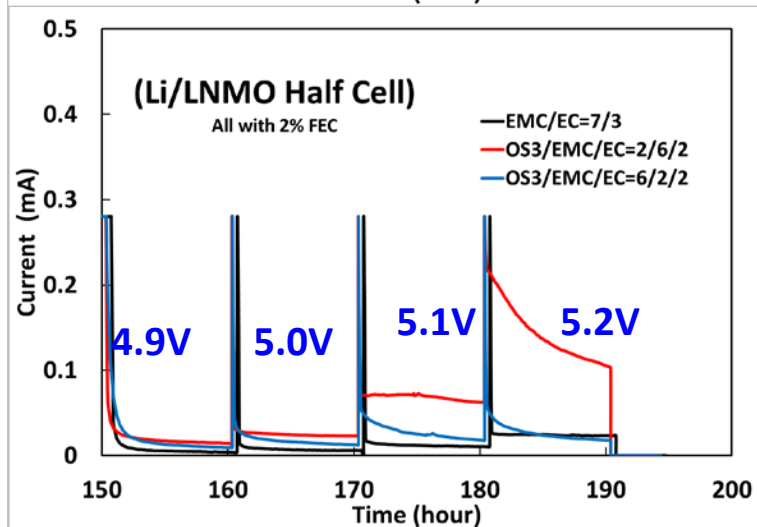
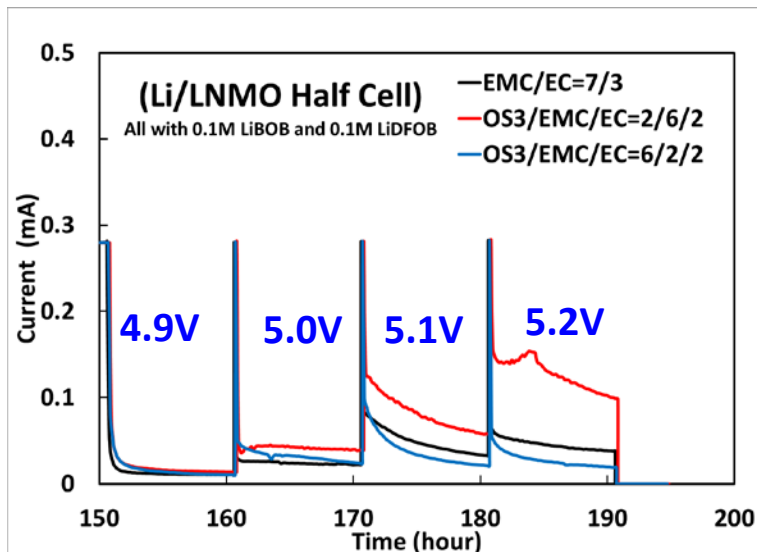


Cycled at C/20 for 2 cycles (3.5-4.9 V) and C/2 for another 10 cycles (3.5-4.9 V).

All additive packages show performance improvement with 60% OS3 formulations, however, FEC is not as good as borate additives.

Technical Progress: Floating Test of OS Formulations (with additives) in Li/LNMO Half Cell

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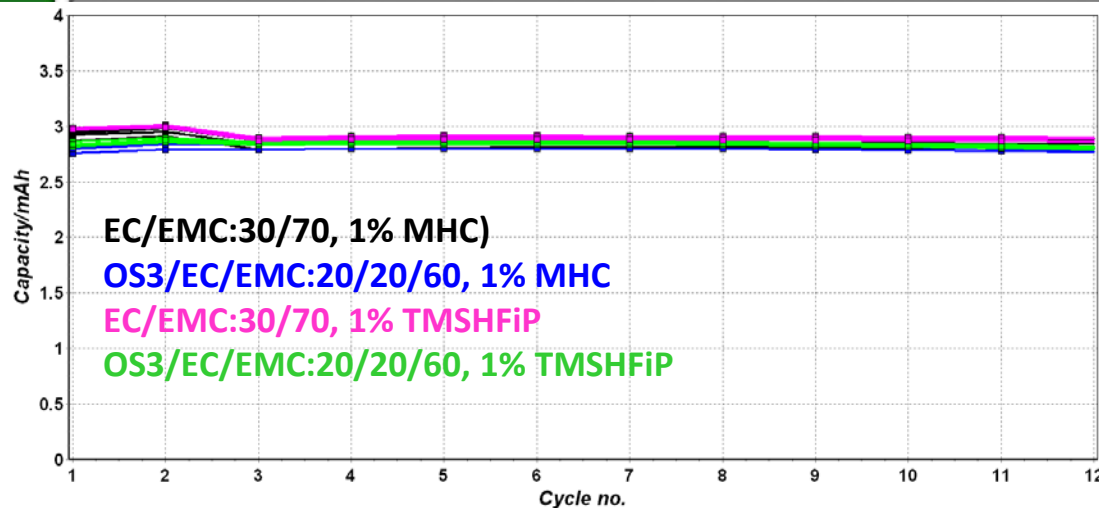


After 12 cycles, cells are charged at C/20 again to 4.9V, then held for 10h at each voltage until 5.2V.

60% OS3 shows better stability overall with different additive packages. FEC is not as good as borate additives in floating tests.

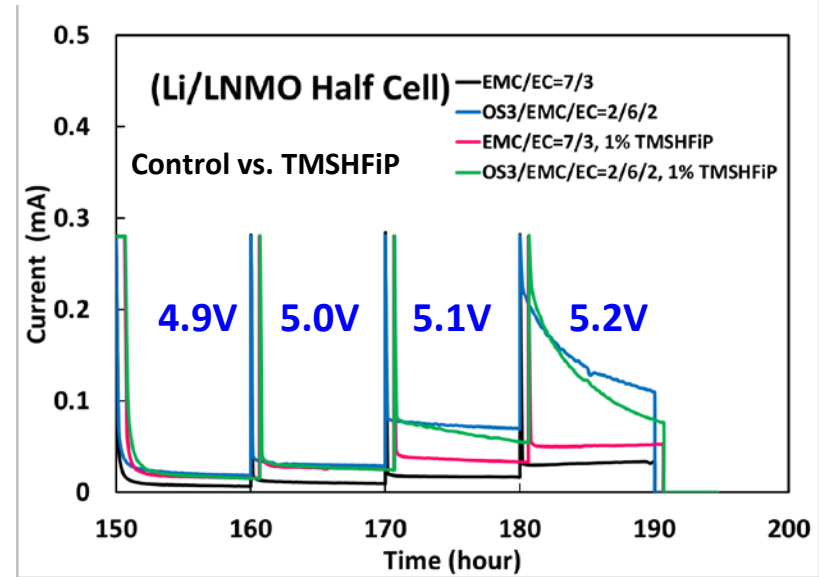
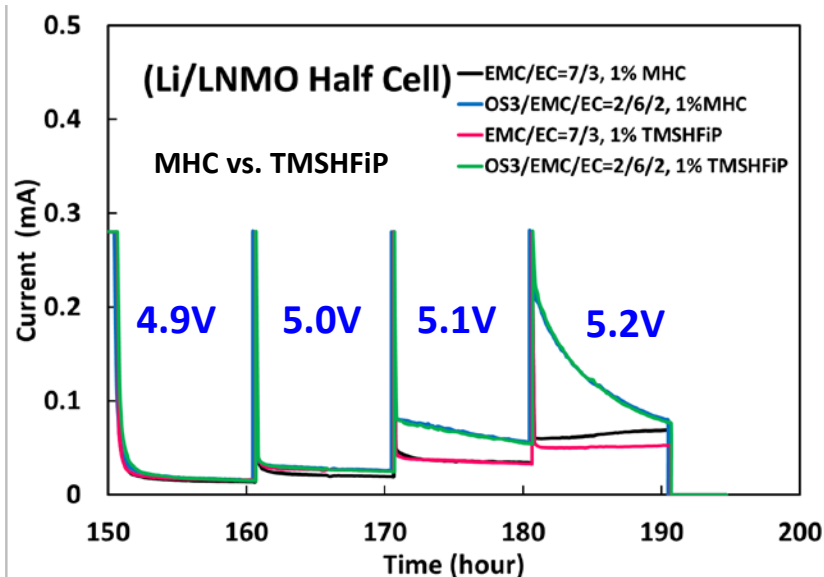
Technical Progress: Initial Evaluation of ARL Additives with OS Solvent

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Cycled at C/20 for 2 cycles (3.5-4.9 V) and C/2 for another 10 cycles (3.5-4.9 V).

No clear difference for ARL additives with 20% OS3.



Summary of Technical Progress

Task 1: Fundamental Mechanistic Studies of New Electrolyte Materials

- Four organosilicon solvents (OS3, OS3a, OS3b, OS3c) in the OS3 family have been successfully synthesized and characterized. OS3 and its analog OS solvents showed great oxidative stability based on LSV and floating test results at Pt electrode both at 30°C and 50°C.
- ARL synthesized eight new additives with bifunctional groups for protection of both anode and cathode surfaces.
- Lithium cobalt phosphate (LCP) cathode has been characterized and shows significantly improved performance, both in terms of discharge profile and cycling stability.

Task 2: Development for Specific HV Systems

- Electrolytes containing 20% OS3 solvent showed higher parasitic current above 4.9V than carbonate control in LNMO/Li cell, which may relate to interaction between OS3 and Li metal anode.
- 60% OS3 containing electrolyte displayed a lower parasitic current than carbonate control at higher voltages (>5V). Electrolyte optimization with different additive packages can enhance cycling performance.

Proposed Future Work

- Silatronix and ARL will continue design and synthesis of new materials for HV applications.
 - New OS solvents/additives will be identified from fundamental understanding of HV electrolyte decay mechanisms
 - Modeling of additives with OS-based electrolyte components will seek to form a robust SEI on the surfaces of HV cathode and graphitic anode.
 - HV solvents and additives will be evaluated with analytical and electrochemical methods
- Silatronix and ARL will continue to optimize the electrolyte formulations for HV system
 - Properties and safety of initial electrolyte formulations will be characterized
 - Electrolyte formulations will be developed with select new materials for the 5V LNMO full cell system for both performance and safety evaluation.
 - 30°C and 55°C cycling tests will begin; floating tests will be extended to full cell; post cell analyses will be conducted
- Top performing HV electrolyte formulations will be tested in 5V LNMO pouch cells (13 layers, 200-300 mAh) at ANL.

Acknowledgements

Contract Support:

- US Department of Energy Office of Energy Efficiency and Renewable Energy (DOE EERE)
- FY 2015 Vehicle Technologies Office Incubator Program
- Award #: DE-EE0007232

Collaborators:

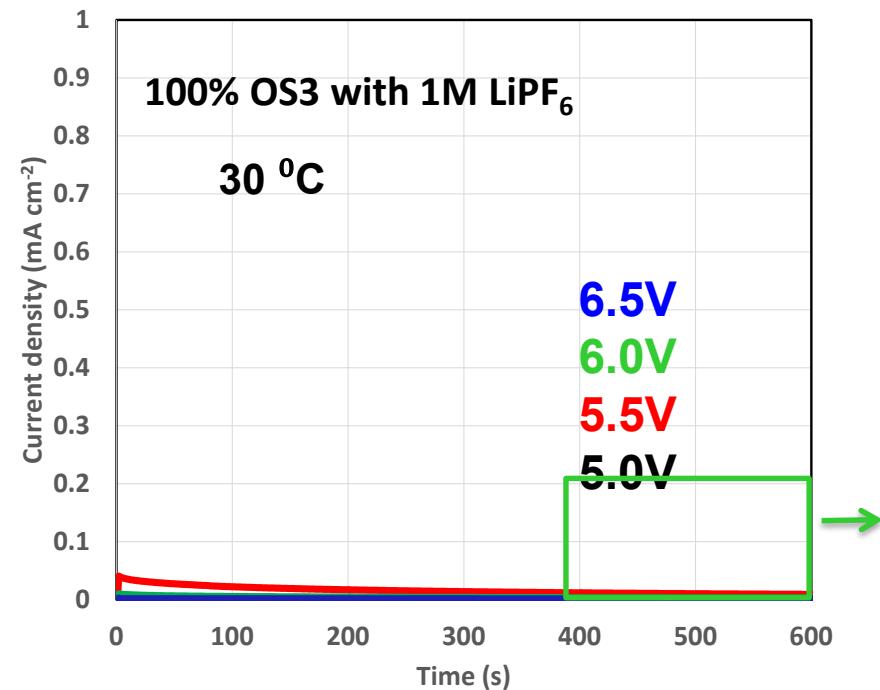
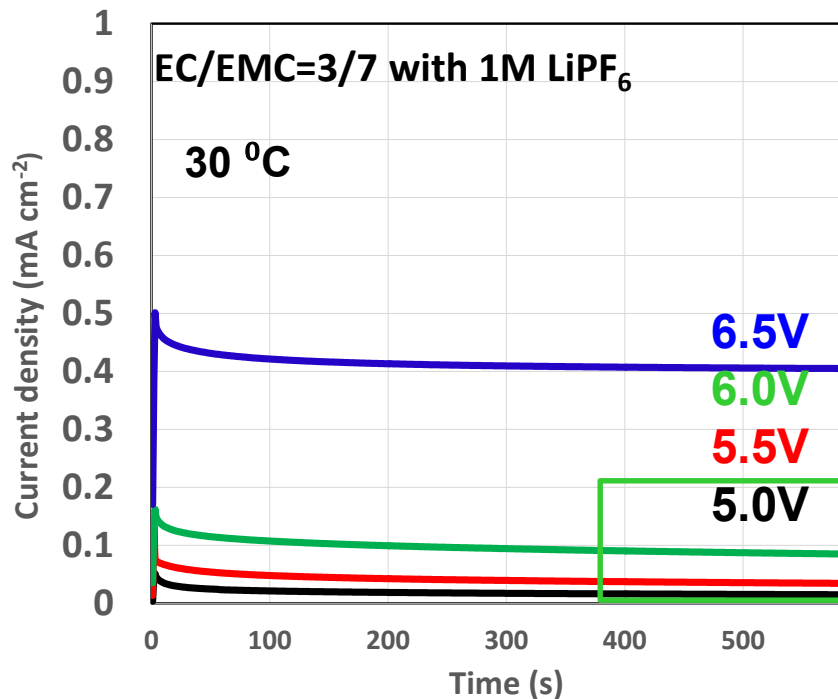
- U.S. Army Research Laboratory (Kang Xu, Project team member)
- Argonne National Laboratory (Bryant Polzin, Project team member)

Questions?

Technical Back-Up Slides

Technical Progress: Floating Test at 30°C

Floating Test of Carbonate control and OS3 at Pt Electrode
(4.5-6.5 V, 10 min at each voltage. Test Condition: 30°C)

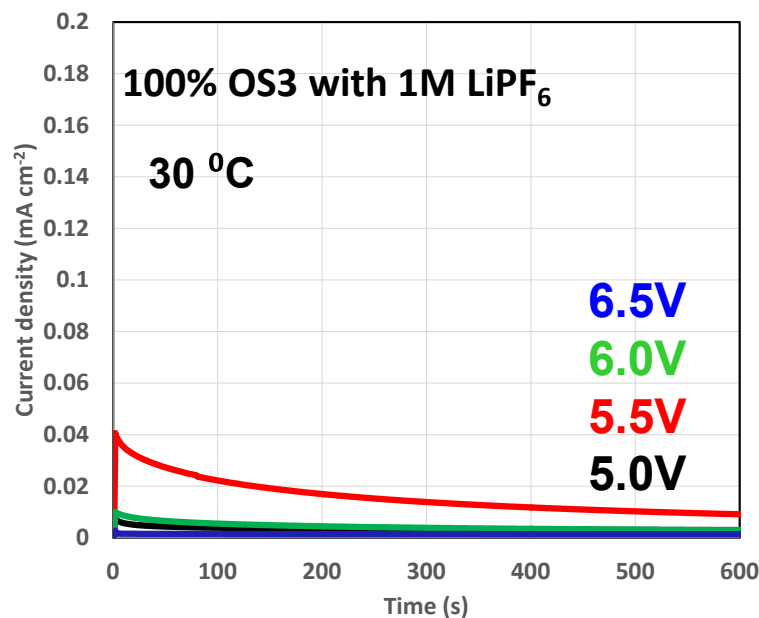


Carbonate control displays much higher parasitic current values than OS3 at higher voltages .

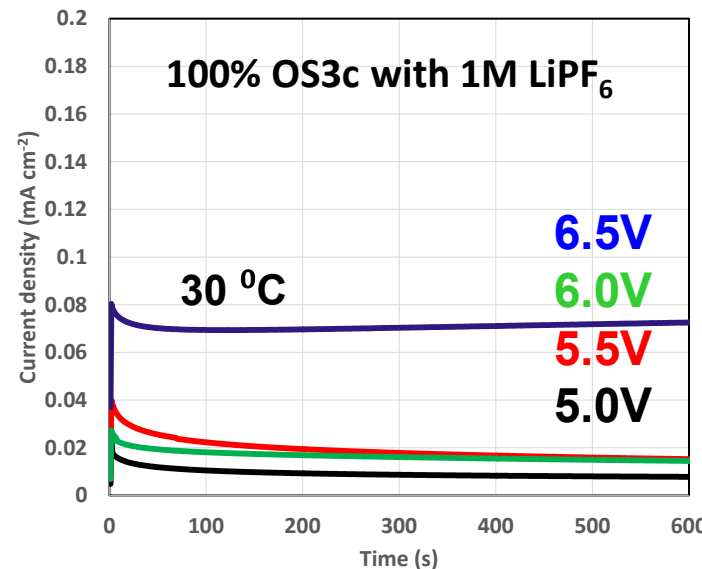
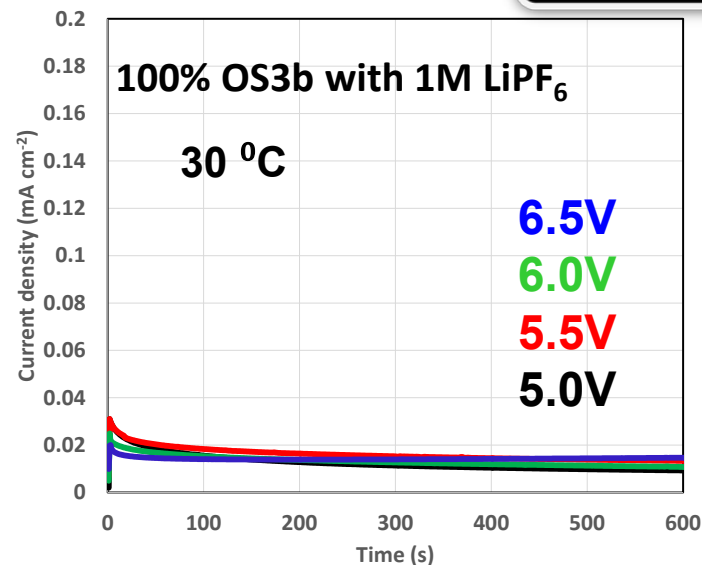
Technical Progress: Floating Test at 30°C

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Floating Test of OS3 Family at Pt Electrode
(4.5-6.5 V, 10 min at each voltage. (Test Condition: 30°C)



Parasitic currents from different OS solvents are all lower than 0.02 mA/cm² at 6 V.



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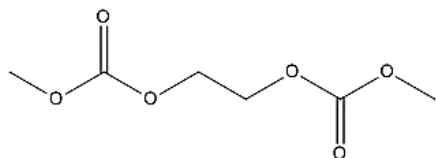
Additive Candidates

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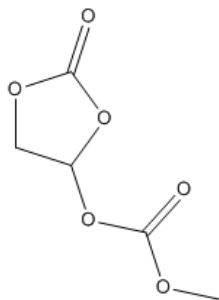
Holistic Design Approach:

Key functional groups effective in forming cathode and anode SEI are synthetically integrated in each additive chemistry

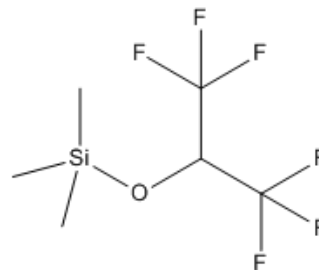
Dimethyl Ester



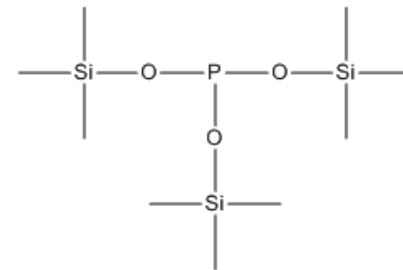
LCC



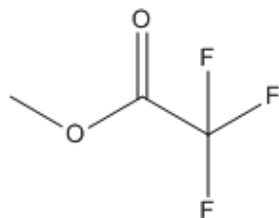
TMSHFIP



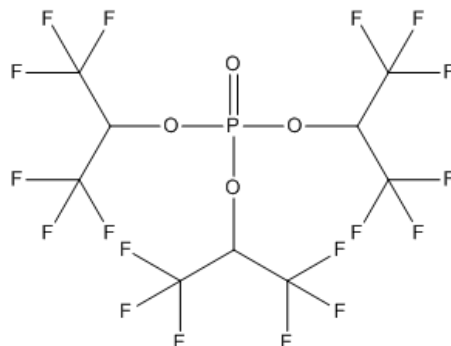
TMSPi



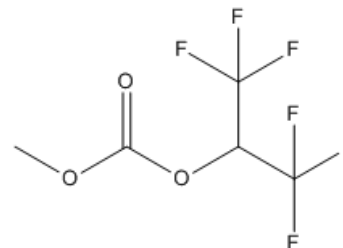
Methyl Trifluoroacetate



HFIP



MHC



PHC

